# Electrochemical Characterization of Chemically Derived Nanocrystalline Cobalt Ferrite Spinel

Subir Kumar Roy and Prashant N. Kumta

Department of Material Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

## **INTRODUCTION**

Oxides containing single transition metals have been reported to be electrochemically active to lithium (1-4). Thackeray et al (1-2) studied the electrochemical insertion of Li ion into Mn<sub>3</sub>O<sub>4</sub> Fe<sub>3</sub>O<sub>4</sub>. Ikeda and Narukawa(3) performed electrochemical studies on Li-CuO primary cells and they showed that the electrochemical discharge process occurs with the reduction of CuO to elemental Cu. Very recently it was reported that CuO and other transition metal oxides e.g.  $Cu_2O$ , CoO, and NiO could reversibly react with lithium resulting in reversible capacities as high as 400mAh/g in the 3-0.2 range(5-6). The mechanism of electrochemical charge-discharge for the transition metal oxides drastically differs from the classical wellknown Li insertion-deinsertion reactions observed in the oxide host structures(7). In the present study we tested the electrochemical activity of a chemically synthesized binary transition metal oxide spinel for the first time.

#### **EXPERIMENTAL**

Nanocrystalline CoFe<sub>2</sub>O<sub>4</sub> samples were prepared by coprecipitating hydroxides of Cobalt and Iron followed by heat treatment in air for 12 hours at 100, 200, 300, 400, 500, 600, 650 and 800<sup>0</sup>C respectively. A hockey puck cell design was used employing lithium foil as an anode and 1M LiPF<sub>6</sub> in EC/DMC (2:1) as the electrolyte. All the batteries tested in this study were cycled for 30 cycles in the voltage range from 0.02~3.0 V employing a current density of 0.25mA/cm<sup>2</sup> and a 60 sec rest period between the charge/discharge cycles using a potentiostat (Arbin electrochemical instrument). The phases present in the ferrite samples and the cycled electrode were analyzed using x-ray diffraction (Rigaku,  $\theta/\theta$  diffractometer) while the microstructure and chemical composition of the electrode was examined using a scanning electron microscope (Philips XL30).

#### **RESULT AND DISCUSSIOIN**

The X-ray diffraction patterns show that all the samples are single-phase cubic spinel. The SEM analyses of the as-prepared powder show that the particles are spherical in shape,  $\approx 10$  nm in size and grow to a size of  $\approx 25$  nm upon heat treatment to 600°C although retaining the spherical shape. The electrochemical analyses of the ferrite samples show that these oxides are active in the 3-0.02V range exhibiting high gravimetric capacities. The capacity as a function of cycle for the electrodes prepared using the heat-treated ferrite samples are shown in Fig. 1. From the capacity vs cycle number plot in Fig.1 it is observed that the fade in capacity for the samples decreases with increasing heat treatment temperature up to 600<sup>0</sup> C. Beyond  $600^{\circ}$ C, the samples exhibit capacity fade, thus indicating that the capacity retention is a function of particle size, which in turn depends on the heat treatment temperature. A stable capacity of ~ 450 mAh/g was obtained after 15 cycles for the  $600^{\circ}$ C heat treated ferrite sample with a critical particle size of 25 nm, suggesting its potential use as an anode material for lithium ion batteries The XRD analyses on the cycled electrodes in Fig.2 show that the discharge process involves the formation of Co-Fe alloy on reduction, which undergoes oxidation on subsequent charge similar to the published report on oxides containing single transition metals. This mechanism drastically differs from the classical well-known Li insertion-deinsertion reaction observed in oxide host structures (7). The Scanning electron microscopy analyses on the cycled electrodes show that the morphology of the electrode materials undergo significant changes during cycling. Results of these studies will be presented and discussed.

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Fig.1. Capacity as a function of cycle for (a) COF100, (b) COF200 (c) COF500, (d) COF600 and (e) COF650 and (f) COF800. [The numbers indicate the heat treatment temperature].



Fig. 2 X-ray diffraction patterns of COF600 coated on Cu foil (a) before cycling (b) after 1<sup>st</sup> discharge (c) after 1<sup>st</sup> charge and (d) after 30 cycles.